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Pesticide Fact Sheet Number 233: Ethylene Bisdithiocarbamates
(EBDCs)

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Pesticide Fact Sheet

Name of Chemical: Ethylene Bisdithiocarbamates (EBDCs)
Reason for Issuance: (Manab, Mancozeb, Metiram, Zineb and Nabam)
Proposed Regulatory Action
Date Issued: December 1989
Fact Sheet Number: 233

DESCRIPTION OF CHEMICALS:

Generic Names: Manganese ethylene bisdithiocarbamate (Maneb);

Zinc ion and manganese ethylene bisdithiocarbamate 80 percent, a coordination product of manganese 16 percent, zinc 2 percent and ethylene bisdithiocarbamate 62 percent (Mancozeb);

Mixture of 5.2 parts by weight (83.9 percent) of ammoniates of [ethylene bisdithiocarbamate]zinc with 1 part by weight (16.1 percent) ethylenebis[dithiocarbamic acid], bimolecular and trimolecular cyclic anhydrosulfides and disulfides (Metiram);

Zinc ethylene bisdithiocarbamates (Zineb);

and disodium ethylene bisdithiocarbamates (Nabam).

Common Names: Ethylene bisdithiocarbamates (EBDCs); Maneb, Mancozeb, Metiram, Zineb, and Nabam

Trade Names: Manzate, Dithane M-22 (Maneb); Dithane M-45, Manzate 200 (Mancozeb); Polyram (Metiram); Dithane Z-78 (Zineb); Parzate, Dithane D-14, Chem Bam, Nabasan (Nabam).

Chemical Abstracts Service (CAS) Nos: 12427-38-2 (Maneb); 8018-01-7 (Mancozeb); 9006-42-2 (Metiram); 12122-67-7 (Zineb); 142-59-6 (Nabam)

Pesticide Type:	Fungicides and biocides
Year of Initial Registration:	Mancozeb 1967, Maneb and Metiram early 1950's, Nabam first use 1935, Zineb first use 1943
U.S. and Foreign Producers:	The principal producers of the EBDC pesticides include Pennwalt Corporation, Rohm & Haas Company, E.I. duPont de Nemours & Company, BASF Corporation, Alco Chemical Corporation and Vinings Chemical Corporation.

USE PATTERNS AND FORMULATIONS:

The ethylene bisdithiocarbamates, the EBDCs, are a group of five pesticides: mancozeb, maneb, metiram, nabam, and zineb. A sixth EBDC, amobam, was cancelled in 1986. In their agricultural uses, the EBDCs are broad spectrum fungicides used to prevent damage to certain fruit, nut, vegetable, field and ornamental crops from fungal diseases. Some EBDC pesticide products have applications as industrial biocides.

Mancozeb is registered for use on apple, asparagus, banana, barley, caprifi, carrot, celery, corn (field, pop- and sweet), cotton, crabapple, cranberry, cucumber, fennel, grapes, melon, oats, onion, papaya, peanuts, pear, pineapple propagation stock, potato, quince, rye, summer squash, sugar beet, tomato and wheat, as well as many ornamentals and tobacco. Mancozeb is registered as a seed treatment on the following: barley, cotton, field corn, flax, oats, peanuts, rice, rye, safflower, sorghum, tomato and wheat.

Maneb is registered for use on almond, apple, apricot, asparagus, banana, beans (green and dried), broccoli, Brussels sprouts, cabbage, carrot, cauliflower, celery, Chinese cabbage, collards, cranberry, cucumber, eggplant, endive, fig, grapes, kale, kohlrabi, lettuce, lima bean, melons, mustard greens, onion, papaya, peach, peppers, potato, pumpkin, rhubarb, spinach, squash, sugar beet, sweet corn, tomato and turnips. Maneb also is registered for use on many ornamentals and tobacco.

The registered food crop uses for metiram are apple, cantaloupe, celery, cotton, cucumber, pecan, potato, and tomato. The only non-food sites for metiram are roses and tobacco.

Zineb is registered on apple, apricot, asparagus, beans (green and dried), beet, blackberry, boysenberry, broccoli, Brussels sprouts, cabbage, carrot, cauliflower, celery, cherries, Chinese cabbage, collards, corn (field and sweet), cranberry, cucumber, currant, eggplant, endive, gooseberry, grapefruit,

grapes, hops, kale, kohlrabi, kumquat, lemon, lettuce, lima bean, lime, loganberry, melon, mushrooms, mustard greens, nectarine, onion, orange, peach, peanut, pear, peas, peppers, plum, potato, prune, pumpkin, radish, raspberry, spinach, squash, strawberry, Swiss chard, tangelo, tangerine, tomato, turnips and wheat. Zineb can also be applied to many ornamental crops and tobacco. Zineb is registered to treat the seed of alfalfa, barley, beans, beet, bluegrass, cantaloupe, clover, crucifers, cotton, cowpeas, cucumber, flax, field corn, oats, peas, peppers, pumpkin, sorghum, soybean, spinach, squash, sugar beet, Swiss chard and watermelon.

Nabam is registered for use on the following industrial sites: air washer water systems, brewery pasteurizers, commercial and industrial water cooling towers, fuel and lubricating oil, storage of hydraulic fluid, leather and leather processing liquors, metalworking cutting fluids, oil recovery drilling fluids and water, preservation in pulp and paper mills, preservation of adhesives and other compounds, pulp and paper mill systems, seawater heat exchangers, and sugar beet and sugarcane processing.

The largest agricultural crop uses of the EBDC pesticides in the U.S. are on potato, apple, cucurbits and tomato. The EBDCs are usually formulated as wettable powders, dusts, concentrates (solutions and suspensions), and granular pellets. There are many application methods including airblast, ground boom, and sprinkler irrigation.

In 1986 the zineb technical registrants cancelled their registrations. At that time, the Agency notified end use suppliers of their lack of a registered supplier. After the first notification in 1986, one end use formulator agreed to support a number of uses. All uses of zineb were suspended by the Agency in July, 1988 when that formulator failed to submit data required under FIFRA section 3(c)(2)(B). In July 1989, that formulator notified the Agency that he wanted to voluntarily cancel his registrations and the Agency issued a second notice about the lack of a registered supplier to the remaining formulaters in October 1989. At the time this document was signed, no formulator had agreed to support zineb registrations. Zineb was used primarily on citrus, apples, mushrooms and pears.

In March 1989, Rohm and Haas, the sole registrant holding nabam agricultural uses, requested that all their agricultural food uses be cancelled. There are no raw agricultural commodity tolerances for nabam (all expressed as zineb). Regulations have been established by the Food and Drug Administration under 21 CFR 173.320 for nabam residues following application to sugar mill grinding, crusher, and/or diffuser systems (secondary direct food additive); and under 21 CFR 176.300 for the use of nabam slimicide added to the process water for the production of paper

and paperboard which will contact food (indirect food additive). Nabam is also registered for use as a biocide at several industrial sites such as in oil drilling fluids and pulp/paper and sugar mills.

On September 6, 1989, all manufacturers of EBDC technical materials for maneb, mancozeb and metiram used on food commodities (Rohm and Haas, duPont de Nemours, Pennwalt and BASF) requested the Agency to amend their registrations to remove 42 of the 55 registered food uses. As to products controlled by these registrants, these registrants will label all their EBDC technical and end use materials manufactured after September 6, 1989, and all their existing EBDC technical stocks and end use products remaining after January 2, 1990, to specify for use only on food commodities as follows: maneb (almonds, bananas, potatoes, sugar beets and sweet corn), mancozeb (asparagus, bananas, cranberries, figs, grapes, onions, peanuts, potatoes, sugar beets, sweet corn, tomatoes and wheat) and metiram (potatoes).

The effect of relabeling the technical products is that it will become unlawful for downstream formulators to use these sources of technical materials in end use products labeled for use on these 42 commodities. The manufacturers have also petitioned the Agency to reduce tolerances for mancozeb on wheat, grapes, peanuts, potatoes and sugar beets. They also notified the Agency that they would not object if the Agency proposed to revoke tolerances for the above-mentioned 42 food uses. Once the registrants' action becomes final, the deleted food uses cannot be reinstated by them until such time as the Agency determines risks associated with these uses are found to be reasonable.

Once the zineb registrations are formally cancelled and the 42 food uses are formally removed from the technical registrants' mancozeb, maneb and metiram labels, the Agency will notify the respective formulators that there is no longer a registered source of technical material for these uses. The Agency's acceptance of these requests is imminent. No use of zineb is likely to remain. If the mancozeb, maneb and metiram formulators want to retain any of the 42 uses, they must both locate an alternative source for the technical and fulfill all data requirements for that technical and the particular end use retained, including those data requirements which are presently the subject of a Data Call-In under FIFRA section 3(c)(2)(B). Failure to take these steps will result in issuance of suspension notices under FIFRA section 3(c)(2)(B). Additionally, in order to get back on the market, any currently suspended registration must be found to comply with the basis for such suspension. In summary, at this time, 55 uses of maneb, mancozeb and metiram remain legally registered by the formulators. If no one supports the 42 uses the technical registrants have deleted from their registrations, eventually only 13 uses will remain. This process

to determine how many uses will remain registered may take several months.

Once the registrants' action becomes final, the deleted food uses cannot be reinstated by them until such time as the Agency determines risks associated with these uses are acceptable.

SCIENCE FINDINGS:

Summary Science Statement: ETU is a common contaminant, degradation product and metabolite of the EBDC fungicides. ETU has been classified by the Agency as a Group B₂ carcinogen (probable human carcinogen). ETU has induced thyroid tumors in rats and liver and thyroid tumors in mice. In addition, ETU has exhibited both developmental and thyroid toxicity in studies with rats.

Toxicology Characteristics:

Subchronic Toxicity:

Oral (rats): ETU caused thyroid effects at the lowest tested level (50 ppm); a NOEL could not be calculated in this test.

NOEL of 5 ppm ETU for thyroid effects in two strains of rats.

Chronic Toxicity:

Carcinogenicity: Liver tumors in mice fed 646 ppm ETU daily.

Liver and thyroid tumors in mice fed 333 or 1000 ppm ETU daily for two years.

Thyroid tumors in rats fed 83 or 250 ppm ETU daily for two years.

Thyroid tumors in rats at 175 and 350 ppm ETU per day.

Thyroid tumors in rats at 250 and 500 ppm ETU; thyroid follicular cell hyperplasia at 5, 25, 125 and 250 ppm.

Developmental Toxicity:

ETU produced delayed development in ossification of the parietal bone; NOAEL ≤5 mg/kg.

Nabam produced major malformations in the brain and increased malformed fetuses in the rabbit at 3, 30 and 60 mg/kg/day.

Mutagenicity:

ETU tested positive in the following assay systems: chromosomal aberrations in bone marrow of mice, UDS-HeLa cells, B. subtilis Rec assay, transformation in BHK 21 cells, and S. cerevisiae-mitotic recombinants. Partial positive in Ames Assay.

Physiological and Biochemical Behavioral Characteristics:

Metabolism: Animal metabolism of the EBDCs is rapid, and ETU and EBIS (ethylene bis-dithiocyanato sulfide) are the major metabolites. ETU has been found in the feces and urine of rats fed mancozeb, the urine of rats fed zineb, and in the urine of mice fed maneb and zineb. ETU administered to cats, rats and mice appears in the urine.

Ecological Characteristics:

Mancozeb and maneb are considered highly toxic to cold water fish; metiram is slightly toxic.

Data submitted by the registrants (not yet reviewed by the Agency) indicate that mancozeb may cause reproductive effects in birds.

Environmental fate data indicate that EBDC parent compounds have the potential to leach into ground water. Retrospective ground water monitoring data for each of the EBDC parent compounds have been required by the Agency.

Tolerance Assessment:

Tolerances have been set for maneb, metiram and zineb at 40 CFR 180.110, 40 CFR 180.217, and 40 CFR 180.115, respectively. Tolerances have been set for mancozeb in 40 CFR 180.176 for raw agricultural commodities and in 40 CFR 185.6300 and 186.6300 for food and feed additives. Nabam food additive tolerances are established in 21 CFR 173.320 and 176.300.

SUMMARY OF REGULATORY POSITION AND RATIONALE

This fact sheet reflects the Agency's proposal to cancel some uses of the EBDC fungicides. On July 17, 1987, EPA

initiated a Special Review of the EBDCs based on the determination that exposure to ETU, a common metabolite, contaminant and degradation product of these pesticides, may pose carcinogenic risks from dietary exposure and developmental and thyroid effects in workers. After a careful review of the benefits associated with the use of the EBDC pesticides and risks associated with the EBDCs and their alternatives, the Agency has proposed a cancellation of registrations or modification to the terms and conditions of registration for uses where risks exceed benefits.

ETU is present as a contaminant of EBDC pesticide products and as part of the residue of the EBDC pesticides on treated agricultural commodities. In addition, a portion of the EBDC residues is converted into ETU in the body after ingestion. The Agency has calculated individual carcinogenic dietary risks for all sites, and developmental and thyroid MOSS for mixer/loader/applicators. Alternatives to the EBDC fungicides exist for most uses, but in most cases are more expensive. As a method of reducing overall risks to a level where the benefits of use outweigh the risks, the Agency is proposing cancellation for some uses of the EBDCs and label language requirements on EBDC products.

All zineb uses are currently suspended, and the only technical registrant has requested voluntary cancellation of its registrations. EPA will be processing this request and determining whether any existing end use product registrant wishes, to attempt to support any of the currently suspended uses. Considering the existing zineb market and apparent lack of current benefits, EPA is proposing to cancel all zineb uses.

On September 6, 1989, the four major registrants of maneb, mancozeb and metiram requested EPA to delete 42 of 55 uses from their registrations. They planned to retain 13 uses. Their action would decrease risk from 4×10^{-4} to 2×10^{-5} . The 13 uses proposed to be retained by the major registrants are almonds, asparagus, bananas, cranberries, figs, grapes, onions, peanuts, potatoes, sugar beets, sweet corn, tomatoes and wheat. The estimated cumulative benefit from these 13 crops is \$14 to \$27 million in producer impacts.

EPA considered the registrants' action and concluded that, while it constituted a major step to reduce dietary risk, it did not go far enough to reduce risks to acceptable levels. Therefore, EPA proposes to retain ten of these 13 crops (almonds, asparagus, cranberries, figs, grapes, onions, peanuts, sugar beets, sweet corn and wheat) and cancel three others (potatoes, tomatoes and bananas). The estimated risks resulting from the ten retained crops would be 3×10^{-6} and estimated benefits would be \$13 to \$26 million in producer impacts.

Because all 55 uses remain on registrations of some formulators, the Agency must address all 55 uses in this Preliminary Determination pending final action by all maneb, mancozeb and metiram registrants. The Agency is proposing to cancel the 42 uses dropped by the technical registrants on the basis of unacceptable risk and a lack of support by the registrants. EPA believes that the action of these major registrants has altered the market sufficiently that it is appropriate to conduct a use-by-use risk/benefit analysis focused only on the use of mancozeb, maneb and metiram on the 13 crops listed above.

The Agency proposes a label language requirement that commercial agricultural workers (M/L/A) applying EBDC pesticides wear coveralls over long-sleeved shirt and long pants, chemical-resistant gloves, shoes, socks, and goggles or a face shield. Additionally, during mixing and loading, a chemical-resistant apron must be worn. For agricultural workers, completely enclosed cabs with positive pressure filtration, or aurally with an enclosed cockpit, a long-sleeve shirt and long pants may be worn in place of the protective clothing described above. Chemical-resistant gloves must be available in the cab or cockpit and worn upon exiting. During aerial application, human flaggers are prohibited unless in totally enclosed vehicles. With incorporation of the above-mentioned protective clothing requirements, MOSS/MOEs for workers using EBDC products on agricultural sites would all increase above 100 except for maneb use on grapes and ornamentals which are proposed for cancellation because EPA has determined that risks exceed benefits.

The Agency proposes a label language requirement establishing an interim reentry interval of 24 hours for all EBDC products used on agricultural sites. This interim reentry interval will remain in effect until dislodgeable foliar residue data (showing EBDC and ETU exposure to agricultural workers reentering treated fields for the purposes of hand harvesting, pruning, weeding, etc.) required in the EBDC Registration Standards and as required in the March 1989 EBDC Data Call-In Notice are submitted and evaluated. These data are due to be submitted in July 1990.

The Agency proposes a label language requirement that homeowners applying EBDC pesticides wear a long-sleeved shirt and long pants and rubber gloves. Gloves must be washed thoroughly with soap and water before removing; clothes must be changed immediately after using the EBDC product and laundered separately from other laundry items before reuse. Homeowners applying EBDCs must shower immediately after use. The Agency did not consider that additional protective clothing requirements for homeowners would be a viable means of reducing risks because the Agency believes that homeowners will not go to the expense of purchasing or wearing protective clothing. Therefore, EPA proposes to

cancel the use of maneb on turf by homeowners where MOSs/MOE's are under 100, and risks outweigh benefits.

In addition, because millions of households have gardens and many more have lawns which could be treated, the Agency is concerned about estimated cancer risks which exceed 10^{-6} for homeowners applying EBDCs. EPA believes such risks exceed the benefits of use. Homeowner sites which have estimated risks exceeding 10^{-6} are: (1) mancozeb on fruit trees and turf and (2) maneb on vegetables, ornamentals, fruit trees and turf. Little or no economic impact is expected because home gardeners can switch from maneb to mancozeb for vegetables and ornamentals and can use captan on fruit trees instead of EBDCs. The Agency estimates that less than one percent of residential lawns are treated with EBDCs and any impact would be negligible. Therefore, EPA proposes to cancel homeowner use of mancozeb on fruit trees and turf, and homeowner use of maneb on vegetables, ornamentals, fruit trees and turf.

The Agency proposes a label language requirement that all industrial workers (M/L/A) applying EBDC pesticides wear coveralls over long-sleeved shirt and long pants, chemical-resistant gloves, shoes, socks, and goggles or a face shield. Additionally, during mixing and loading, a chemical-resistant apron must be worn. Similar label language already appears on nabam labels and OSHA requires protective clothing when applying hazardous chemicals under 29 CFR §1910.132.

The Agency proposes cancellation of nabam use in paper mills and sugar mills based on thyroid MOSs/MOE's below 100 due to occupational exposure after incorporation of protective clothing requirements listed above and carcinogenic dietary risk from nabam use in sugar mills.

Within 90 days of the issuance of this document, the Agency intends to propose tolerance revocations for the 45 food uses of maneb, mancozeb and metiram and all (58) food uses of zineb proposed for cancellation in this Preliminary Determination. The Agency intends to finalize the tolerance actions, reflecting consideration of public comments, when all products containing such products are voluntarily cancelled, or the Agency issues the Final Determination, whichever occurs earlier. In issuing the final rule to revoke tolerances, the Agency will set tolerance expiration dates which take into consideration any crops which were treated legally before the effective date of the cancellation. Section 408 tolerances for retained uses will be reevaluated once the Agency receives metabolism and residue data required under the EBDC Comprehensive Data Call-Ins and Registration Standards. Any necessary adjustments to raise or lower existing tolerances will be proposed at that time. No new 409 tolerances need to be established for the uses the Agency is proposing to retain, based on data available at this time.

The implementation of these proposals would result in the cancellation of registrations for the following 45 food crops: apple, apricot, banana, barley, beans, broccoli, brussels sprouts, cabbage, cantaloupe, carrot, casaba melons, cauliflower, celery, collards, corn (field and pop), cotton, crabapple, crenshaw melons, cucumbers, eggplant, endive, fennel, honeydew, kale, kohlrabi, lettuce, lima beans, mustard greens, nectarines, oats, papaya, peach, pear, pecan, pepper, pineapple, pumpkin, potato, rhubarb, rye, spinach, squash, tomato, turnip, and watermelon. The non-food sites proposed for cancellation are: maneb on commercial ornamentals, homeowner turf, homeowner ornamentals, homeowner fruit trees and homeowner vegetables; mancozeb on homeowner turf and homeowner fruit trees; and zineb on commercial ornamentals and turf. The industrial sites proposed for cancellation are paper mills and sugar mills.

The following registrations for food crops and seed treatments would be retained under the proposed action: maneb on almonds, sugar beets and sweet corn and mancozeb on asparagus, cranberries, figs, grapes, onions, peanuts, sugar beets, sweet corn and wheat. Registrations which would be retained for non-food sites included: metiram on homeowner roses; mancozeb on commercial ornamentals and turf and nabam uses in brewery pasteurizers, in fuel oil, in oil well drilling fluids, in leather processing, in metal working cutting fluids, as preservatives (in adhesives, animal glues, inks, latex, mineral slurries, paints and coatings), and in seawater heat exchangers.

SUMMARY OF MAJOR DATA GAPS

The following data submissions have been required under the authority of FIFRA section 3(c)(2)(B) in an October 1988 Data Call-In:

Retrospective ground water monitoring data for each of the EBDC parent compounds due February 1992.

Additional rat and mouse onco studies for maneb due November 1990; onco rat and mouse studies for metiram due June 1990.

The following data submissions have been required under the authority of FIFRA section 3(c)(2)(B) in an April 1987 Data Call-In:

Additional rat and mouse onco studies for mancozeb and nabam due June 1991.

The following data submissions have been required under the authority of FIFRA section 3(c)(2)(B) in a March 1989 Data Call-In:

Tank-mix stability data are due in December 1989.

Dermal exposure data for nabam are due in March 1990.

Dermal absorption data for maneb, zineb and their ETU degredates are due in March 1990.

Reentry protection data and use practice information are due in July 1990.

EBDC and ETU residue monitoring data are due in September 1990.

In the PD 2/3 for the EBDCs, the Agency based estimates for dietary risk on the best available data, and yet EPA acknowledged that dietary risk estimates could conceivably be lowered one or two orders of magnitude when supported by a well-designed and well-conducted residue monitoring study and use information. In addition, assumptions about dermal absorption and tank-mix stability may have resulted in overestimates of mixer/loader/applicator developmental and thyroid risks. Risk estimates may be lowered when all the required studies are received and reviewed by the Agency.

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